

## **NON-ISOTHERMAL KINETICS: ART, DEBATE OR JUST APPLIED SCIENCE**

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Almost ten years ago, I considered it interesting enough to formulate a dozen or so of the most pertinent questions on non-isothermal kinetics, trying consequently to give then an exhaustive answer [1]. I was happy to witness the first enthusiastic and naturally created discussion during the 6th ICTA in Bayreuth in 1980, which resulted in the unanswered question "What can we do?" (to be understood as "How can we improve the present state of the art?"). As the programme chairman of the 8th ICTA in Bratislava in 1985 and aware of the controversial situation, I insisted upon the inclusion of non-isothermal kinetics among the specialized workshops, which latter resulted in the formation of the ICTA Kinetics Subcommittee and the formulation of topics and goals to be considered [2], thanks to its chairman, J. H. Flynn from Washington, who has pioneered advances in this topics since 1960. Today I was presented at a continuation of such round-table discussions on kinetics at ESTAC 4 in Jena, and I found that I was embarrassed and pleased at the same time. A new young generation of well-trained kineticists proved themselves capable of holding the reins of kinetic power, among them E. V. Boldyreva and V. B. Okhotnikov from Novosibirsk, M. Maciejewski from Warsaw and J. Málek from Pardubice. They showed certain degree of skepticism, however, pointing out mainly the negative sides of non-isothermal kinetics. In most of the contributions we could hear the same type of questions time and time again [1], reappearing from one discussion to another, and often resembling the questions published almost 25 years ago in the excellent, but somehow rather neglected book of one of the pioneers of non-isothermal kinetics, P. D. Garn [3]. In this context, I should like to remind you of his statement that a reaction never obeys the equations we propose, and that the kinetic functional dependences are to be solved like a crossword-puzzle. Substances are not aware of any theories, either isothermal or non-isothermal, and they react as they like under thermal conditions according to their own physico-chemical processes, and not as we propose. This does not mean, however, that we have to damn all previous kinetic data, and particularly the questionable value of activation energy as a non-essential parameter. The purpose

of our experimentation is in particular to determine certain numerical values, whatever we call them, trying our best to compare them with one another, although this is often not possible. The kinetics itself is not responsible for such a complicated situation. In fact, we should blame ourselves for using a tricky form, the experimental, which is a very plastic function associated with many different drawbacks (such as its constants, mutual correlation, etc.). The desirable fitting of a straight line to a logarithmic plot can equally be reached by an advanced statistical computer procedure or simply by manually redrawing the points on a transparent sheet of paper as many times as they require to get close enough to the proposed line. In this respect, the computer is an insensitive tool, having no "physical or chemical soul" at all. Such a vague kinetic description often requires veiling by resonant or ingenious mathematics (e.g. the popular  $p(x)$  function), which is sometimes unnecessary and sometimes very nice to exemplify thermal analysis as the art of science. However, it does offer a little help, as we do not yet know a better form to express a thermally activated process on the basis of distribution statistics and/or probability attempts. Furthermore, the everyday use of computers has created a new level of kinetic evaluations quickly producing all the necessary and unnecessary numerical data which were earlier too difficult to obtain because of the time-consuming treatment. We must again bear in mind that a computer never knows more than an experimentator and that it can be a very patient and faithful servant in carrying out stupid procedures. Statistics is the best example to show a rather arbitrary use of ready-made (library) procedures while often violating the basic premises (normal distribution, etc.) under which the algorithm was compiled. A certain primitiveness of kinetic evaluations can be located even in expensive software accessoried to very sophisticated all-computerized TA instruments. Heterogeneous and particularly solid-state kinetics offers many specialized equations as well as methods allowing us to distinguish between a great variety of possible reactions. Single-valued measurements produced by the majority of TA instruments are not relevant enough to carry out such advanced studies unless associated with complementary observations. However, spot, morphological studies are often incompatible with averaged TA data, not to speak about the problems of mathematical modelling. Here we arrived at a dilemma: Are the mechanistic data of direct observations on gradually quenched samples of better quality than the averaged data obtained by the relatively much simpler and temperature-detecting method of continuous TA? There is another question of whether it is meaningful to oversimplify heterogeneous kinetics by introducing single-valued data into a corresponding single-valued kinetic equation: Is this merely a mathematical exercise, or does it even have a certain physical and/or applicative value? Could mere TA data help us to distinguish something in heterogeneous kinetics without direct evidence? If not, should we stop this? The

same applies to isothermal and non-isothermal measurements. Though we can prove the equality [4] of isothermal and non-isothermal phenomenological treatments, we can adopt the concept of the uselessness of TA for providing a better understanding of the physics and chemistry of heterogeneous reactions [2]. Should we stop going on with non-isothermal kinetics based on mere TA data, or would it be a pity to avoid such a traditional and, in my personal opinion, perspective field of science, making itself an evident part of its art? We should admit that every method has its positive merits as well as its disadvantages, associated with its mathematical treatment and inherent in its given type of instrumentation. Problems associated with dynamic kinetic measurements, however, have a general significance in many branches of experimental kinetics (including even traditional equilibrium thermodynamics in the evaluation of "kinetic" and metastable phase diagrams [5] of non-equilibrated materials), because truly constant and experimentally prerequired conditions are hard, if not impossible to achieve. It is now time to make progress with these problems of dynamic measurements with distinctions, or otherwise we should simply give up. It is easy to criticize the inadequacy of the present state of non-isothermal kinetics, but it is much more difficult to foretell its developments and/or to establish a new, as yet non-traditional approach. We are all looking forward to this; it may happen as suddenly as the discovery of novel high-temperature ceramic superconductors. At any rate, we have to see the advances as a vital goal of our future kinetic workshops and I advocate their detailed preparation to avoid flat discussions; this should preferably be realized through strong chairmanship at subsequent ICTA conferences.

## References

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- 3 P. D. Garn, *Thermoanalytical Methods of Investigation*, Academic Press, New York, 1964.
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